Molecular Structure of *meso* Tetra(2,4,6-trimethoxyphenyl)porphyrin, A Free Base Precursor of a 'Bis-pocket' Iron Complex

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The crystal structure of the free base *meso* tetra(2,4,6-trimethoxyphenyl)porphyrin indicates that the bulky *meso* substituents form 'pockets' on both faces of the porphyrin plane 2.27 Å deep and 9.74 Å on the diagonal between *o*-methoxy oxygen atoms on the same face.

The involvement of high-valent iron in the oxygen transfer reactions of cytochrome P450 has stimulated efforts to generate high valent porphinatoiron complexes in synthetic model systems.[1] A number of *meso* tetra-arylporphinatoiron complexes[2—7] in which the porphyrin *meso* carbon atoms and the two faces of the iron atom are protected within pockets formed by bulky aryl *meso* substituents have been synthesized. The tetramesityl complex was successfully utilized in generating an oxoferryl porphyrin cation radical.[7,8] In addition to stabilizing the reactive oxo complex, bulky *meso* substituents may serve to elucidate stereochemical interactions between catalyst and substrate during the oxygen transfer reaction. The currently favoured mechanism for epoxidation of alkenes requires the side-on approach of an alkene parallel to the porphyrin plane[9] and as a result, non-bonded interactions with the pocket would be expected to cause epoxidations to be highly sensitive to alkene stereochemistry. Verification of the proposed mechanism by comparison of product profiles for variously substituted alkenes demands that the steric constraints imposed by the pocket be well defined, hence, the dimensions and geometry of the pockets of synthetic oxygen transfer catalysts are of considerable interest. We report the molecular structure of *meso* tetra(2,4,6-trimethoxyphenyl)porphyrin [TPP(2,4,6-OMe)H_2], the free base precursor of a hindered 'bis-pocket' porphyrin. Since insertion of iron would be expected to produce no important changes in porphyrin geometry, this structure provides an estimate of the size and geometry of the pockets of the corresponding iron complex and can serve as a model for studies on its oxygen transfer catalysis.

The free base was synthesized and purified by conventional methods[10,11] and gave u.v.-visible[2] and ^{1}H n.m.r. spectra consistent with the desired structure: u.v.-visible (CH_2Cl_2) $\lambda_{max.}$($\varepsilon \times 10^{-4}$) 419(31.1), 512(2.5), 545(1.4), 590(1.1), and 650(0.9) nm; ^{1}H n.m.r. (250 MHz, $CDCl_3$), 8.70[s, 8H, pyrrole (py)-βH], 6.54(s, 8H, m-H), 4.08(s, 24H, *o*-OMe),

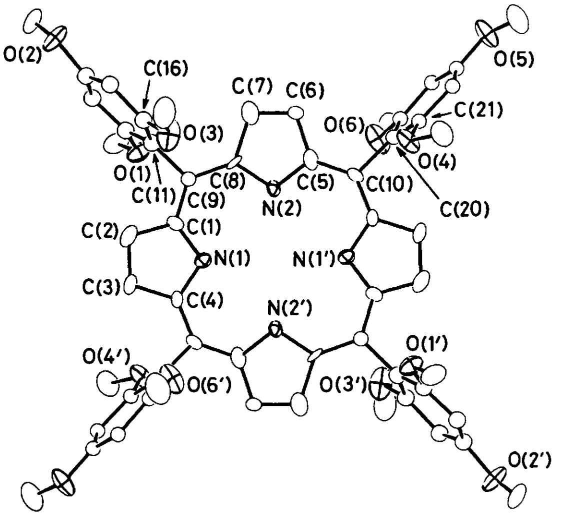

Figure 1. View of the molecule; the viewing direction is perpendicular to the porphyrin mean plane. Primed and unlabelled atoms are related to unprimed atoms by inversion through the centre.

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3.46(s, 2H, *p*-OMe), and −2.50(s, 2H, py-NH). Small single crystals of a hydrate marginally acceptable for *X*-ray crystallographic analysis were obtained on slow evaporation of a chloroform–heptane solution. *Crystal data*: $C_{56}H_{54}N_4O_{12} \cdot H_2O$, M = 993.1, monoclinic, space group $P2_1/c$, a = 13.762(6), b = 14.187(9), c = 14.190(11) Å, β = 98.36(5)°, U = 2741(5) $Å^3$, Z = 1, D_c = 1.203, D_m = 1.24. Intensity data were collected by the ω–2θ scan method using an Enraf-Nonius CAD4 diffractometer equipped with Mo-K_α radiation and a graphite monochromator. The structure was solved by direct methods and refined by full-matrix least-squares methods. The final value of the R factor is 0.097 for 885 independent observations with $I > 2.5\sigma(I)$. The hydrogen atoms on the pyrrole nitrogen atoms and the water molecule were not located.

A projection of the molecule is given in Figure 1; the two halves of the molecule are related by a crystallographic inversion centre at the centre of the porphyrin ring. The porphyrin ring is approximately planar, with no atom deviating from the plane defined by N(1)–N(2)–C(1)–C(10) by more than 0.072(2) Å. The phenyl rings are also planar and are nearly perpendicular to the porphyrin plane. The torsion angles defined by C(1)–C(9)–C(11)–C(16) and C(5)–C(10)–C(20)–C(21) are 103° and 99° respectively, and the interplanar dihedral angles between the porphyrin plane and the corresponding phenyl ring planes at C(9) and C(10) are 102° and 98°. The bond lengths and angles in the structure are in no way unusual.‡

A cavity is defined by the *ortho* oxygen atoms O(1′), O(4), O(3), O(6′) forming the top and the symmetry-related oxygen atoms O(1), O(4′), O(3′), O(6) forming the bottom. The cavity is divided into two pockets by the plane of the porphyrin ring. The depth of the pockets from the oxygen atoms to the porphyrin plane varies from 2.13(1) Å for O(3) to 2.43(1) Å for O(6), and is, on average 2.27 Å. The edges of each pocket bounded by the oxygen atoms vary from 6.54 to 7.16 Å, while the diagonals across the openings [exemplified by O(1′)–O(3)] are in the range 9.73—9.75 Å.

In a putative oxoferryl porphyrin cation radical the Fe–O bond length is estimated to be 1.7 Å with a 0.25 Å displacement of the iron atom from the porphyrin plane assumed on the basis of MO calculations,[12—14] suggesting that the reactive oxo ligand of the oxygen transfer species derived from the title compound would be contained within the pocket (*ca.* 2 Å above the centre of the porphyrin plane). Based on the geometry of this model, epoxidation by the complex should be highly sensitive to the substitution patterns of the substrates in a side-on approach, with oxidation of the *cis* alkenes favoured over *trans* because of the required projection of a *trans* substitutent into the confined pocket. Precisely this type of steric effect has been reported[9] to account for regioselectivity of epoxidations catalysed by iron tetramesitylporphyrin, closely related in structure and geometry to the trimethoxy-substituted tetraarylporphyrin described here.

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‡ The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Rd., Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.